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Supporting Information

Direct Analysis of Metal Ions in Solutions with High Salt Concentrations by Total Reflection X-ray Fluorescence (TXRF)

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Calculation of the Sensitivity factors after calibration of the TXRF spectrometer S2 PICOFOX™ molybdenum.

The sensitivity factors (S_i) were calculated according to the Eq. (S1), where C_{IS} is the concentration of the internal standard (100 mg L^{-1} of gallium), N_i is the net pulse number of counts in the measured spectrum of the analyte i (counts), S_{IS} is the relative sensitivity of the internal standard element (1 by convention), N_{IS} is the net pulse number in the measured spectrum of the internal standard (counts) and C_i is the measured concentration of the analyte i. The input data came from measuring 10 calibration solutions in duplicate, which were equally prepared two by two; i.e., five different calibration points. These calibration solutions consisted of multi-element standards containing in all the solutions 100 mg L^{-1}of gallium and in each one of the calibration solutions 5, 15, 50, 100 or 200 mg L^{-1}, respectively. Therefore, the calculated S_i were obtained by a 4-data average for each five calibration point. All measurements lasted for 1000 s.

$$S_i = \frac{C_{IS} \cdot N_i \cdot S_{IS}}{N_{IS} \cdot C_i} \qquad \text{(S1)}$$

As part of the calibration, the elemental concentrations obtained after measuring (C_i) were normalized (C_{Ni}) by dividing them by a correction factor, calculated as the average concentration of the analyte measured in the corresponding blanks (C_B) divided by the calculated theoretical concentration of the analyte ($C_{T,B}$) (Eq. S2).

$$C_{Ni} = \frac{C_i}{C_B/C_{T,B}} \qquad \text{(S2)}$$

TXRF spectra that depict the number of counts vs. the characteristic energy of each element
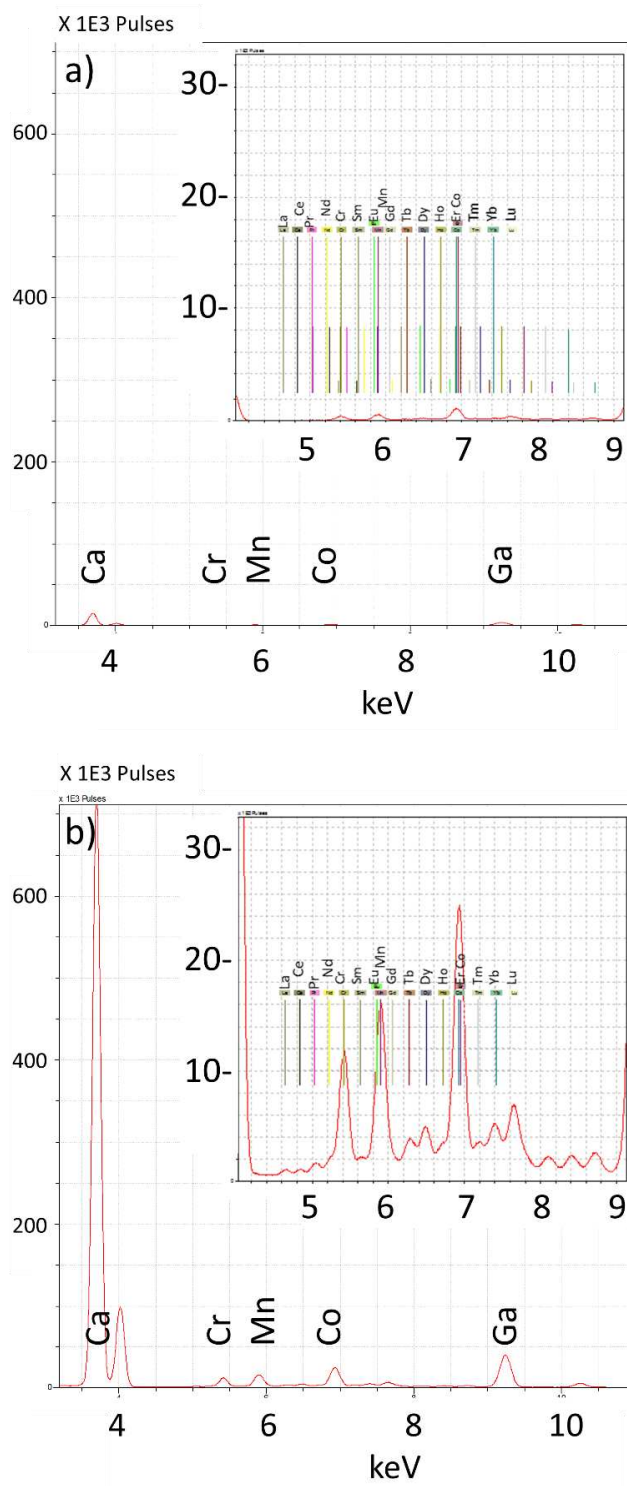
Figure S1. Number of counts depicted in the spectra of the 5 μL-solution sampled on the carrier when dissolving with a) MilliQ water or b) an aqueous solution of Triton™ X-100, 53.50 g L^{-1}. The final composition is 0.005 M of 20 analyte elements with 0.980 molar ratio between the matrix element CaCl$_2$ and the analytes (27.75 g L^{-1} of CaCl$_2$).

Photos of the carriers after TXRF measurements
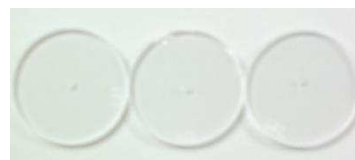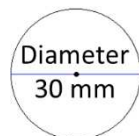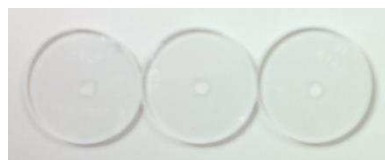
a) Solution of 53.5 g L^{-1} of Triton^{TM} X-100.　　　　Solution without Triton^{TM} X-100
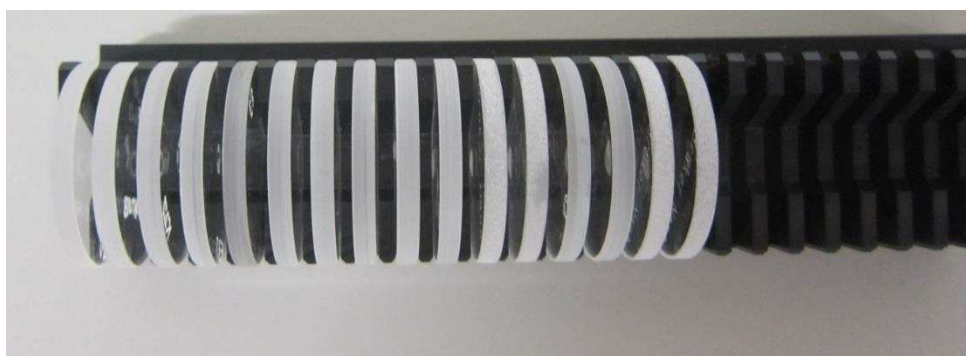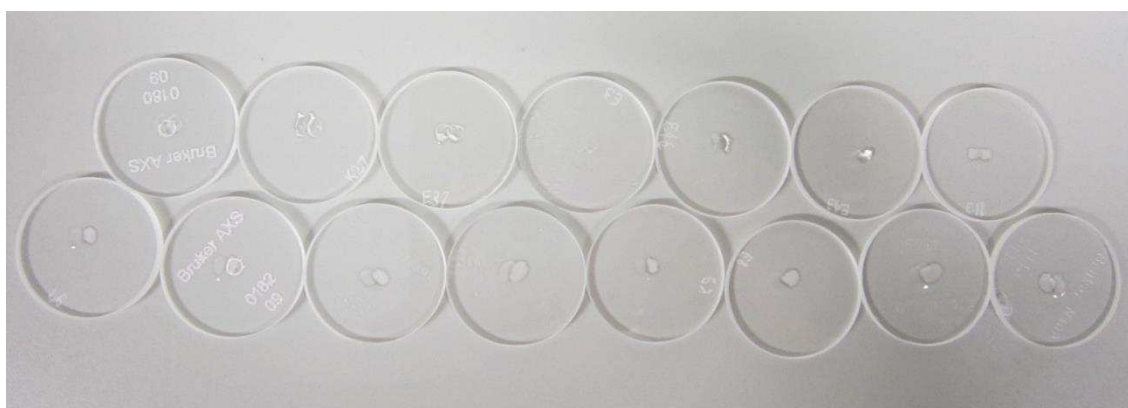
b) Solution with 53.5 g L^{-1} of Triton^{TM} X-100

Figure S2. a) Appearance of the dried 5-µL sample deposited on the carriers after TXRF measurements with and without a 53.5 g L^{-1} solution of Triton^{TM} X-100 in water. b) The matrix is uniformly distributed over a bigger (top b)) and thinner (bottom b)) surface on the carrier when using Triton^{TM} X-100, obtaining reproducible drops on the carrier.

Table S1. Recovery rates (average from duplicates) of 20 elements using nine different internal standards with no matrix of CaCl₂. The solution contains in total 0.005 M of 20 elements from standard solutions: 50 mg L⁻¹ of Cr, Mn, Co, Ga and Sr, and 10 mg L⁻¹ of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. No Triton™ X-100 was added in the internal standardization.

Y Lα 14.958	Lu Lα 7.656	Yb Lα 7.416	Tm Lα 7.180	Er Lα 6.949	Ho Lα 6.720	Dy Lα 6.495	Tb Lα 6.273	Gd Lα 6.057	Eu Lα 5.846	Sm Lα 5.636	Nd Lα 5.2304	Pr Lα 5.0337	Ce Lα 4.8402	La Lα 4.65097	Sr Kα 14.165	Ga Kα 9.25174	Co Kα 6.93032	Mn Kα 5.89875	Cr Kα 5.41472	←Analyte, X-ray radiation / Internal standard, IS (X-ray radiation)↓
86	90	99	99	99	89	103	92	96	69	108	97	107	91	102	89	97	99	94	■	Cr (Kα 5.41472)
92	95	105	105	106	94	109	104	100	87	95	109	110	106	103	95	100	106	■	102	Mn (Kα 5.89875)
90	93	103	103	103	92	106	95	99	72	113	101	111	95	106	92	101	■	98	105	Co (Kα 6.93032)
90	93	103	103	103	92	107	95	100	72	113	101	112	95	106	93	■	103	98	105	Ga (Kα 9.25174)
99	103	114	114	114	102	118	105	110	79	124	111	123	105	117	■	112	114	108	116	Sr (Kα 14.165)
80	83	93	92	92	83	96	85	89	64	101	90	■	85	95	83	91	92	88	94	Pr (Lα 5.0337)
89	92	102	102	102	91	106	95	99	71	112	■	111	94	105	92	100	102	97	104	Nd (Lα 5.2304)
97	101	112	112	112	■	116	103	108	78	122	110	121	103	115	101	110	112	107	114	Ho (Lα 6.720)
87	90	100	100	■	90	104	93	97	70	110	98	108	92	103	90	98	100	95	102	Er (Lα 6.949)

Average ± standard deviation of all: 99.4 ± 10.7%   n.d., not detected.

Table S2. Recovery rates average from duplicates of 20 elements (50 mg L^{-1} of Cr, Mn, Co, Ga and Sr, and 10 mg L^{-1} of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) using nine of them as internal standards; in a 5.55 g L^{-1} CaCl$_2$ (0.910 mole fraction). No Triton™ X-100 was added in the internal standardization.

Y Lα 14.958	Lu Lα 7.656	Yb Lα 7.416	Tm Lα 7.180	Er Lα 6.949	Ho Lα 6.720	Dy Lα 6.495	Tb Lα 6.273	Gd Lα 6.057	Eu Lα 5.846	Sm Lα 5.636	Nd Lα 5.2304	Pr Lα 5.0337	Ce Lα 4.8402	La Lα 4.65097	Sr Kα 14.165	Ga Kα 9.25174	Co Kα 6.93032	Mn Kα 5.89875	Cr Kα 5.41472	← Analyte, X-ray radiation / Internal standard, IS (X-ray radiation) ↓
233	191	173	161	182	141	147	121	119	90	137	96	96	75	73	235	200	157	116	■	Cr (Kα 5.41472)
199	164	150	140	158	123	129	106	104	80	120	85	85	67	65	201	172	137	■	90	Mn (Kα 5.89875)
145	121	113	106	118	93	98	81	78	62	92	66	66	52	52	146	127	■	78	69	Co (Kα 6.93032)
113	97	94	88	97	77	82	69	65	54	78	58	58	46	47	114	■	85	66	60	Ga (Kα 9.25174)
101	88	87	81	89	71	76	64	60	51	73	55	55	44	45	■	91	79	62	56	Sr (Kα 14.165)
253	205	184	170	195	149	155	128	126	94	144	100	■	78	74	256	216	167	122	107	Pr (Lα 5.0337)
253	206	184	171	195	150	156	128	126	94	144	■	100	78	74	256	216	167	122	107	Nd (Lα 5.2304)
157	131	122	114	128	■	105	88	84	67	99	72	71	56	56	159	137	111	84	75	Ho (Lα 6.720)
121	102	96	90	■	79	84	70	67	54	79	58	58	46	46	122	106	88	67	60	Er (Lα 6.949)

Average ± standard deviation of all: 110.6 ± 49.5%   n.d., not detected.

Table S3. Recovery rates average from duplicates of 20 elements (50 mg L^{-1} of Cr, Mn, Co, Ga and Sr, and 10 mg L^{-1} of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 55.49 g L^{-1} CaCl$_2$ (0.990 mole fraction). No Triton™ X-100 was added in the internal standardization.

Y Lα 14.958	Lu Lα 7.656	Yb Lα 7.416	Tm Lα 7.180	Er Lα 6.949	Ho Lα 6.720	Dy Lα 6.495	Tb Lα 6.273	Gd Lα 6.057	Eu Lα 5.846	Sm Lα 5.636	Nd Lα 5.2304	Pr Lα 5.0337	Ce Lα 4.8402	La Lα 4.65097	Sr Kα 14.165	Ga Kα 9.25174	Co Kα 6.93032	Mn Kα 5.89875	Cr Kα 5.41472	←Analyte, X-ray Radiation / Internal standard, IS (X-ray radiation)↓
820	252	182	255	265	140	71	**106**	n.d.	143	68	n.d.	n.d.	n.d.	n.d.	1300	624	227	129	■	Cr (Kα 5.41472)
649	201	148	205	211	**111**	57	**84**	n.d.	**105**	50	n.d.	n.d.	n.d.	n.d.	1029	495	179	■	81	Mn (Kα 5.89875)
371	**114**	83	**116**	**120**	63	32	48	n.d.	62	30	n.d.	n.d.	n.d.	n.d.	587	282	■	58	46	Co (Kα 6.93032)
133	41	30	42	43	23	12	17	n.d.	23	11	n.d.	n.d.	n.d.	n.d.	211	■	37	21	17	Ga (Kα 9.25174)
64	20	14	20	21	11	6	8	n.d.	11	5	n.d.	n.d.	n.d.	n.d.	■	49	18	10	8	Sr (Kα 14.165)
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Pr (Lα 5.0337)
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Nd (Lα 5.2304)
588	181	131	183	190	■	51	76	n.d.	**103**	49	n.d.	n.d.	n.d.	n.d.	931	447	162	93	73	Ho (Lα 6.720)
311	**95**	68	**96**	■	53	27	40	n.d.	57	27	n.d.	n.d.	n.d.	n.d.	492	236	86	49	38	Er (Lα 6.949)

Average ± standard deviation of all: 93.9 ± 192.4%   n.d., not detected.

Table S4. Recovery rates average from duplicates of 20 elements (50 mg L^{-1} of Cr, Mn, Co, Ga and Sr, and 10 mg L^{-1} of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 97.11 g L^{-1} CaCl$_2$ (0.994 mole fraction). No Triton™ X-100 was added in the internal standardization.

← Analyte, X-ray Radiation / Internal standard, IS (X-ray radiation) ↓

Lu Lα 7.656	Yb Lα 7.416	Tm Lα 7.180	Er Lα 6.949	Ho Lα 6.720	Dy Lα 6.495	Tb Lα 6.273	Gd Lα 6.057	Eu Lα 5.846	Sm Lα 5.636	Nd Lα 5.2304	Pr Lα 5.0337	Ce Lα 4.8402	La Lα 4.65097	Sr Kα 14.165	Ga Kα 9.25174	Co Kα 6.93032	Mn Kα 5.89875	Cr Kα 5.41472	Cr Kα 5.41472	IS
424	259	261	179	230	194	163	**116**	n.d.	**91**	**121**	n.d.	n.d.	n.d.	n.d.	1385	628	214	111	■	Cr (Kα 5.41472)
0	0	0	0	0	0	145	**112**	n.d.	**82**	**122**	n.d.	n.d.	n.d.	0	0	579	197	■	91	Mn (Kα 5.89875)
203	**125**	**124**	**84**	**111**	**93**	80	56	n.d.	45	56	n.d.	n.d.	n.d.	n.d.	663	300	■	53	47	Co (Kα 6.93032)
68	42	43	29	38	32	27	18	n.d.	15	19	n.d.	n.d.	n.d.	n.d.	224	■	35	18	16	Ga (Kα 9.25174)
30	19	20	14	19	15	13	8	n.d.	6	8	n.d.	n.d.	n.d.	n.d.	■	47	16	9	7	Sr (Kα 14.165)
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Pr (Lα 5.0337)
n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Nd (Lα 5.2304)
227	136	135	**93**	**114**	■	**83**	64	n.d.	48	68	n.d.	n.d.	n.d.	n.d.	728	327	111	58	51	Ho (Lα 6.720)
821	382	422	388	■	280	71	268	n.d.	39	453	n.d.	n.d.	n.d.	n.d.	2346	995	335	160	152	Er (Lα 6.949)

Average ± standard deviation of all: 105.0 ± 255.4%

n.d., not detected.

Table S5. Recovery rates average from duplicates of 20 elements (50 mg L^{-1} of Cr, Mn, Co, Ga and Sr, and 10 mg L^{-1} of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y), using nine of them as internal standards; in a 138.73 g L^{-1} CaCl$_2$ (0.996 mole fraction). No Triton^{TM} X-100 was added in the internal standardization.

← *Analyte, X-ray Radiation*

Internal standard, IS (X-ray radiation) ↓

IS (X-ray radiation)	Y Lα 14.958	Lu Lα 7.656	Yb Lα 7.416	Tm Lα 7.180	Er Lα 6.949	Ho Lα 6.720	Dy Lα 6.495	Tb Lα 6.273	Gd Lα 6.057	Eu Lα 5.846	Sm Lα 5.636	Nd Lα 5.2304	Pr Lα 5.0337	Ce Lα 4.8402	La Lα 4.65097	Sr Kα 14.165	Ga Kα 9.25174	Co Kα 6.93032	Mn Kα 5.89875	Cr Kα 5.41472
Cr (Kα 5.41472)	455	241	226	189	n.d.	267	144	**105**	**113**	120	n.d.	n.d.	n.d.	160	n.d.	1527	622	223	109	■
Mn (Kα 5.89875)	0	0	0	0	0	0	**113**	**80**	159	**94**	n.d.	n.d.	n.d.	224	0	0	563	0	■	99
Co (Kα 6.93032)	203	109	**120**	**86**	n.d.	**102**	55	43	76	46	n.d.	n.d.	n.d.	**107**	n.d.	689	283	■	50	49
Ga (Kα 9.25174)	72	39	44	31	n.d.	37	20	14	29	17	n.d.	n.d.	n.d.	41	n.d.	245	■	37	18	18
Sr (Kα 14.165)	30	16	19	13	n.d.	16	9	5	13	7	n.d.	n.d.	n.d.	18	n.d.	■	894	15	7	8
Pr (Lα 5.0337)	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Nd (Lα 5.2304)	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	■	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ho (Lα 6.720)	1913	984	809	698	n.d.	n.d.	54	899	336	45	n.d.	n.d.	n.d.	475	n.d.	6736	2581	894	455	401
Er (Lα 6.949)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Average ± standard deviation of all: 157.1 ± 599.9%   n.d., not detected.